

# STRUCTURAL STUDIES OF THE EXCIPLEX TYPE OF TETRACENE/CHRYSENE AND TETRACENE/DIBENZO(A,H)ANTHRACENE

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## ABSTRACT

*Spectroscopic properties of mixed aggregates of the guest/host: tetracene/chrysene and tetracene/dibenzo(a,h)anthracene were studied in n-alkane colloidal solutions in water and crystallized mixed films at low temperature. Low guest concentration resulted in the observation of sensitized fluorescence, whereas at high guest concentration, emission of a new exciplex type was seen. The theoretical work of Stevens concerning the correlations of donor-acceptor molecular orbitals was considered in order to interpret the structure of the newly observed exciplex.*

**Keywords:** chrysene, dibenzo(a,h)anthracene, exciplex, MO correlations, tetracene

## INTRODUCTION

The interaction between polycyclic aromatic hydrocarbon (PAH) molecules has been the subject of a large number of investigations (Stevens, 1971; Powell & Soos, 1975; Amine *et al.*, 1991). The interesting work by Davydov (1962; 1964) based on the exciton model provided a good interpretation for the absorption spectra in pure crystals. The most interesting result of 'Davydov' splitting revealed the importance of the interaction between PAH molecules.

The study of the absorption spectra allows the possibility of investigating the spectroscopic behavior of the association of the molecules if the obtained species are sufficiently stable. This was seen in the case of dimer formed in solid media (Chandross *et al.*, 1966), or more complex formed in viscous media at low temperature (Martinaud & Kottis, 1978).

In most cases, the observed interaction between PAH molecules is not assigned to the ground state but to an excited state of the complex. Furthermore, significant evidence was observed for the formation of excimer (Turro & Kuo, 1987; Daeubler *et al.*, 1994,1997; Seko *et al.*, 1998) or exciplex-type emission (Amine *et al.*, 1991; Desvergne *et al.*, 1987; Mataga, 1997).

The spectroscopic properties of the PAH interactions in alkane matrices at low temperature have shown that the low solubility of aromatics in n-alkanes induces, during cooling, a high local concentration. They have also exhibited a non-uniform distribution of solute molecules (aggregates and pseudocrystallites). These aggregates have a significant effect on the spectroscopic properties; in particular, when a guest molecule is added, mixed aggregates can result.

In the present work, we have studied the guest/host: tetracene/chrysene (Tet/Chry) and tetracene/dibenzo(a,h)anthracene (Tet/DBA) in n-octane at low temperature (Shpolskii solution). As a result, emissions of exciplex type were observed.

Note that the same type of emission was also observed in mixed aggregates formed in colloidal solutions in water and in mixed crystallized films.

From a theoretical point of view, it is considered convenient to investigate the experimental results using Stevens' theory (Stevens, 1988) in order to explain the newly obtained type of association between aromatic molecules.

## EXPERIMENTAL PROCEDURE

Fluorescence spectra at 4.2 K were obtained with a home-made fluoremeter built from commercial components (Soulignac & Lamotte, 1987). Excitation was provided by a Xenon lamp (Osram 450 W) whose light was dispersed through a Jobin Yvon HRS monochromator equipped with a 1200 lines/mm grating. The fluorescence emission was observed at 90° through the same type of monochromator as for excitation. The solution to be studied was contained in a 4 mm O.D. 30mm long fused silica tube attached at its top end to a stainless steel rodlike holder which fits inside a liquid helium cryostat (MERIC), thus allowing rapid change of samples. Best reproducibility of the cooling rate was obtained by first immersing this assembly (sample tube plus holder) into a dewar containing liquid nitrogen. The sample holder was then introduced quickly into the helium cryostat after complete cooling of the solution to 77 K.

For the preparation of colloidal suspension, 0.1 ml of concentrated aromatic solutions in tetrahydrofuran (THF) was injected in 20 ml of distilled water.

In order to obtain crystallized mixed films the same concentrated aromatic solutions in THF were used. Then a few droplets of this solution were placed on a thin sheet of quartz. After the slow evaporation of THF, at room temperature, mixed crystallized films were obtained whose mean thickness is estimated to be less than 1  $\mu\text{m}$ .

The n-octane used as solvent (FLUKA, spectroscopic grade) was kept on molecular sieves (10 Å). It was verified to be free of any undesirable fluorescence. High purity zone refined DBA, chrysene and tetracene were employed.

## RESULTS

### Mixed aggregates prepared in Shpolskii solutions

Figure 1 shows the fluorescence spectra of mixed aggregates of chrysene (host, concentration  $5 \times 10^{-5}$  M) and tetracene (guest, concentration  $C_t$ ) in polycrystalline n-octane solution at a temperature of 5 K and an excitation wavelength of 335 nm.

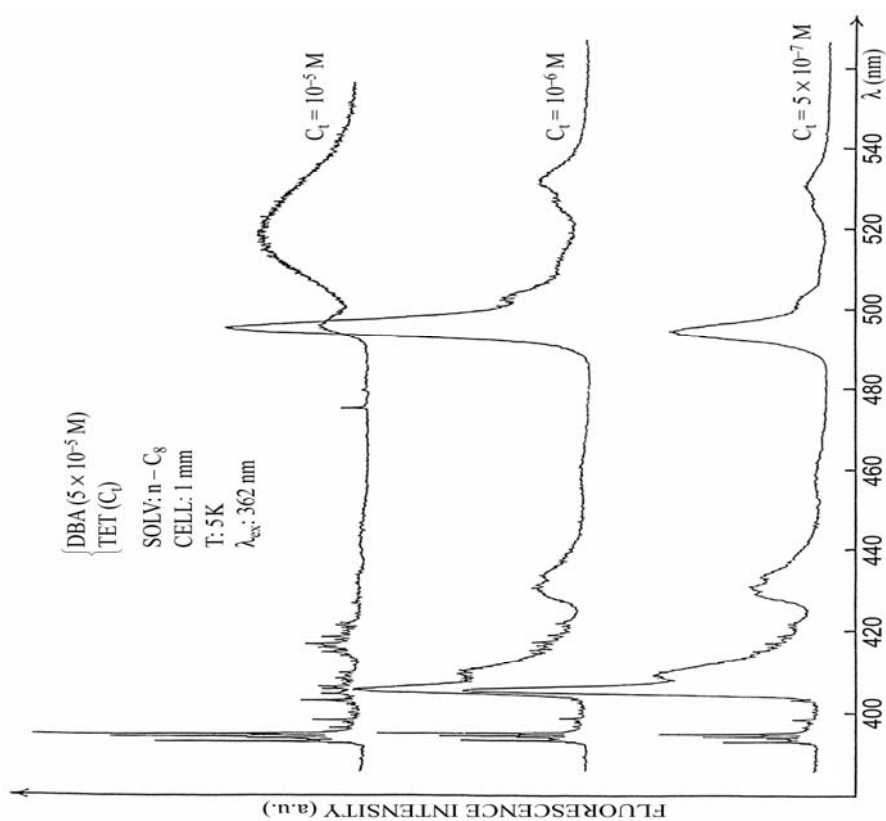
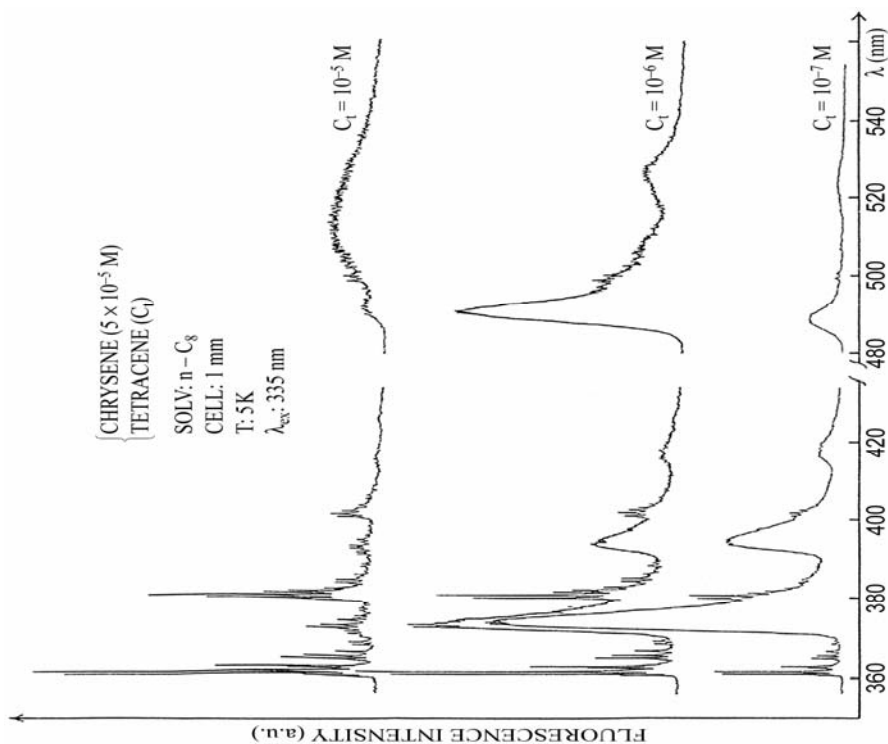


Figure 1. Sensitized fluorescence spectra of tetracene/chrysene mixed aggregates formed in n-octane at 5 K. The chrysene concentration is fixed at  $5 \times 10^{-5}$  M but that of tetracene is variable ( $C_t$ ). The gaps shown have no effects.

At a low concentration of tetracene ( $C_t=10^{-7}$  M) the sensitized fluorescence of tetracene (called S emission), detected at about 490 nm, is supported by the flow of energy and the exciton migration to guest molecules included in the host aggregates. For relatively higher concentration of tetracene ( $C_t=10^{-6}$  M), the S emission increases considerably and at the same time the aggregate spectrum of chrysenes, at about 375 nm, decreases as compared with that of the low concentration one.

For a still higher concentration of tetracene ( $C_t=10^{-5}$  M), the S emission almost disappears and a broad structureless fluorescence spectrum (named X emission) is shown in the low energy part (between 500 to about 540 nm) and the aggregate spectrum of chrysenes completely disappears.

Using the same guest (tetracene), a different host: DBA was investigated in the same way. Figure 2 shows the resulting spectra which indicate that S emission occurs at low concentration of tetracene and X emission at high concentration of tetracene.



**Figure 2.** Sensitized fluorescence spectra of tetracene/DBA mixed aggregates formed in n-octane at 5 K. The DBA concentration is fixed at  $5 \times 10^{-5}$  M but that of tetracene is variable ( $C_t$ ).

It is to be noted that the quasi-line spectra of the host in both figures remain unchanged.

#### Mixed aggregates prepared as colloidal suspension in water

The emission spectra of the mixed aggregates prepared as colloidal suspension in water were obtained at a temperature of 77 K. They showed S and X emissions, the former at low concentration and the latter at high concentration of tetracene. It is worth mentioning here that similar observations as above result from the mixed aggregates formed in cooled n-octane. Figure 3 is a spectral example of mixed aggregates of DBA and tetracene. In this figure, the X type emission ( $\lambda \approx 520$  nm) is well observed at a very high concentration ( $C_t=10^{-5}$  M); S emission is observed at all concentrations but is maximum at the lowest one ( $C_t=10^{-7}$  M). A similar effect is observed for mixed chrysene and tetracene aggregates in water (Amine *et al.*, 1991).

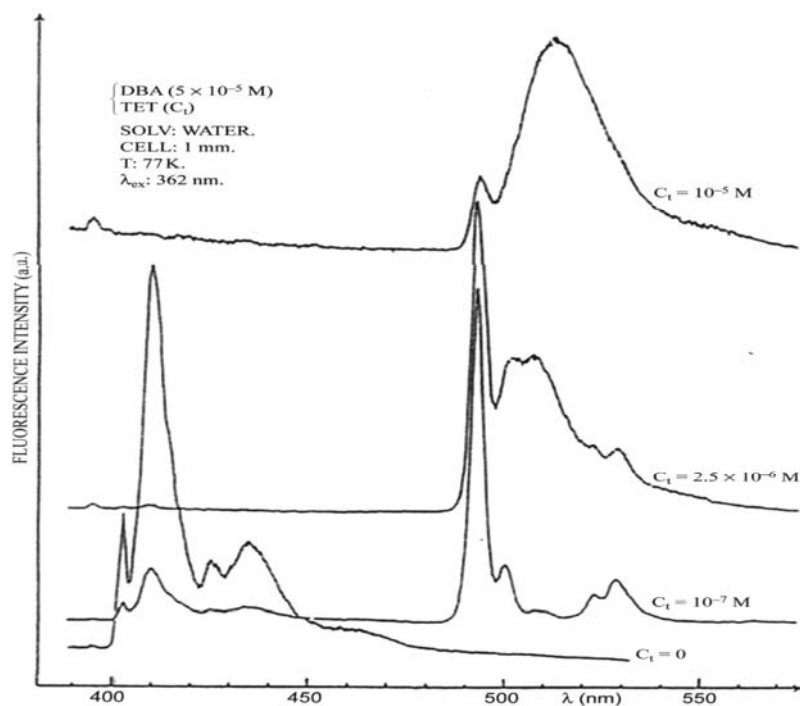
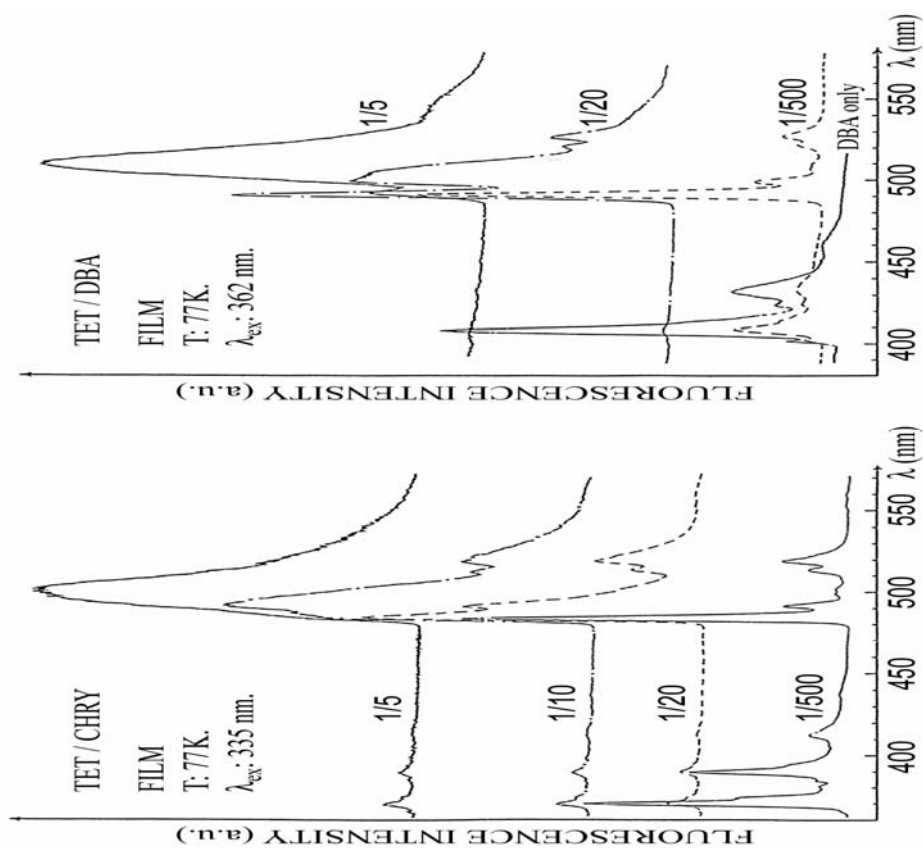


Figure 3. Sensitized fluorescence taken at 77 K, spectra of tetracene/DBA mixed aggregates formed in water and at different concentrations of tetracene.

### Crystalline mixed films of Tet/Chry and Tet/DBA

Figure 4 represents the fluorescence spectra obtained using mixed crystalline films of Tet/Chry and Tet/DBA respectively. It can be seen from this figure that similar results were obtained as explained in mixed aggregates formed in water. The fractions shown on this figure are due to the ratio of concentrations of guest/host prepared in THF.



**Figure 4.** Sensitized fluorescence spectra of mixed crystallized films of Tet/Chry and Tet/DBA at different proportions of tetracene (mol of guest/mol of host) and at 77K.

## DISCUSSION

All the observed spectra offer a good opportunity to investigate the appearance of the X type emission spectrum. Reabsorption effects and formation of some guest aggregates from the use of a large concentration of the guest are shown not to affect the obtained X-type emission for the following reasons:

- i- The possibility that the wide spectrum corresponds to tetracene aggregates is easily eliminated as no proper fluorescence of these aggregates is observed from the concentrated solution in n-C<sub>8</sub>.
- ii- The possibility of a spectral deformation in n-octane due to reabsorption is equally rejected because we have checked that the fluorescence spectrum of tetracene was not affected by the reabsorption at high concentration.

It is to be noted that the excitation spectra of sensitized fluorescence (S and X) are formed from the superposition of the molecular spectrum of tetracene in the chrysene aggregates and of the spectrum of chrysene aggregates alone. This result shows that the sensitized emission leads to a transfer of energy from the inside of the chrysene aggregates towards the tetracene molecules trapped in those aggregates.

The broad X emission seems to result from the formation of a complex. Since the absorption spectrum of this complex remains unchanged, therefore its occurrence at the ground state is not stable, and thus the hypothesis of an exciplex formation seems to be the most probable.

Examination of the crystalline structure by X-ray diffraction revealed that none of our guest/host couples Tet/Chry and Tet/DBA are formed of isomorphous elements.

At low concentrations of the guest and in spite of the fact that the lattice had suffered a deformation due to the introduction of dopant molecule, the dominant configurations are most probably very close to those found in the pure host crystal.

When the concentration of the dopant molecules is increased, the perturbation generated by these molecules implies a radical modification to the crystalline structure. In this case, favorable configurations for the formation of a complex are created either inside the specific defect of crystal or by the appearance of new crystalline phases.

The above discussion results from the fact that the guest molecules cannot be substituted for the host molecules without causing a perturbation to the crystal lattice. This

shows that the occurrence of a cofacial structure is most probable as it will be indicated by Stevens' theory.

### THEORETICAL APPROACH AND APPLICATIONS

#### Theory

Stevens (1988) suggested a qualitative description of a 1:1 cofacial structure to study the stability of eventual complex formation between organic molecules. The method is based on the correlations between donor-acceptor molecular orbitals in order to determine if the complex can be obtained at the ground state (EDA-complex) or at the excited state only (exciplex).

The intermolecular orbitals (IMO)  $\psi_i$  may be considered as a linear combination of donor ( $\varphi_i$ ) and acceptor ( $\theta_i$ ) molecular orbitals (MO) belonging to the same representation of the point group defining the intermediate cofacial complex (HOMO:  $\varphi_1, \varphi_2$  and  $\theta_1, \theta_2$ ; LUMO:  $\varphi_1^*, \varphi_2^*$  and  $\theta_1^*, \theta_2^*$ ). These IMO are of predominantly donor ( $\psi_D, \psi_D^*, \dots$ ) or acceptor ( $\psi_A, \psi_A^*, \dots$ ) character.

The highest occupied and lowest unoccupied IMO in the complex ground state are labeled  $\psi_D, \psi_A$  and  $\psi_D^*, \psi_A^*$  respectively, while primed symbols refer to IMO of lower ( $\psi_A', \psi_D'$ ) or higher ( $\psi_D^{*'}, \psi_A^{*'}$ ) energy in the general sequence:

$$\psi_A' < \psi_D' < \psi_D < \psi_A < \psi_A^* < \psi_D^* < \psi_D^{*' < \psi_A^{*'}$$

Sixteen singly excited zeroth-order configurations are available of which:

- eight arising from electron promotions of the type  $\psi_D \longrightarrow \psi_D^*$  (or  $\psi_A \longrightarrow \psi_A^*$ ) are designated as locally excited (LE) states of the form  $|AD^*\rangle$  (or  $|A^*D\rangle$ ),
- eight are of the charge transfer (CT) origin insofar as they involve electron promotions of the type  $\psi_D \longrightarrow \psi_A^*$  (or  $\psi_A \longrightarrow \psi_D^*$ ) and are described by  $|A^-D^+\rangle$  (or  $|A^+D^-\rangle$ ).

These sixteen excited zeroth-order configurations with their promotional origins are listed in Table 1.

**TABLE 1**  
Excited zeroth-order configurations obtained by electron promotions  $\psi_i \longrightarrow \psi_j^*$

$\psi_i^*$	$\psi_A^*$	$\psi_D^*$	$\psi_A^{*'}$	$\psi_D^{*'}$
$\psi_I$				
$\psi_D$	$ A^-D^+\rangle$	$ AD^*\rangle$	$ A^+D^-\rangle$	$ AD^*\rangle$
$\psi_A$	$ A^*D\rangle$	$ A^+D^-\rangle$	$ A^*D\rangle$	$ A^+D^-\rangle$



$\Psi_D^+$	$ A^-D^{*+}\rangle$	$ AD^{*+}\rangle$	$ A^+D^{*-}\rangle$	$ AD^{*-}\rangle$
$\Psi_A^+$	$ A^+D^-\rangle$	$ A^-D^-\rangle$	$ A^{*-}D^-\rangle$	$ A^+D^{*-}\rangle$

The ground state of the complex at zeroth-order is represented by the totally symmetric  $|AD\rangle$  configuration. The interpretation of the first-order requires an interaction between  $|AD\rangle$  and totally symmetric excited zeroth-order configurations. This brings a stabilisation by configuration interaction (CI) with regard to separated molecules. The CT configurations bring out in particular the most important stability to molecular complexes.

### Applications

In Table 2, we have summarized the symmetry point group of DBA, chrysene and tetracene molecules considered in this work. The symmetries and the energies (calculated by the SCF-MO (Dewar & Trinajstić, 1970)) of the two highest occupied molecular orbitals (HOMO) and the two lowest unoccupied molecular orbitals (LUMO) are also listed with their respective properties.

**TABLE 2**  
**Symmetries (Sym) and energies (E) of the two HOMO and the two LUMO of PAH molecules concerned in this work.**

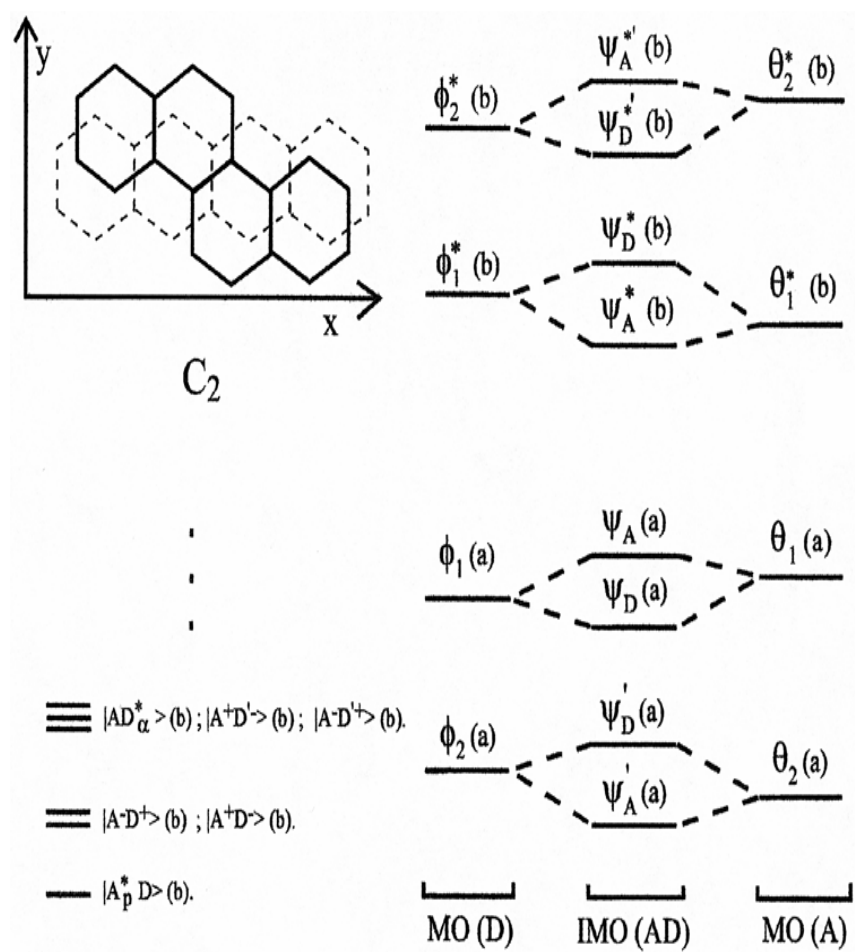
	Group of Symmetry	HOMO		LUMO					
		Sym	E(eV)	Sym	E(eV)				
DBA	$C_{2h}$	$b_g$	1.432	$b_g$	1.751	$a_u$	9.380	$a_u$	9.698
Chry	$C_{2h}$	$a_u$	1.229	$a_u$	1.620	$b_g$	9.510	$b_g$	9.901
Tet	$D_{2h}$	$b_{1u}$	1.008	$a_u$	2.209	$b_{2g}$	8.921	$b_{3g}$	10.122

Since tetracene and chrysene (or tetracene and DBA) belong to the  $D_{2h}$  and  $C_{2h}$  symmetry point groups respectively, therefore a cofacial structure of Tet/Chry or Tet/DBA may belong to a common subgroup  $C_2$ ,  $C_s$  or  $C_i$ . A cofacial structure of  $C_s$  or  $C_i$  is not applicable due to the absence of a plane of symmetry and inversion centre respectively. Thus the only possible complex is that of  $C_2$  symmetry.

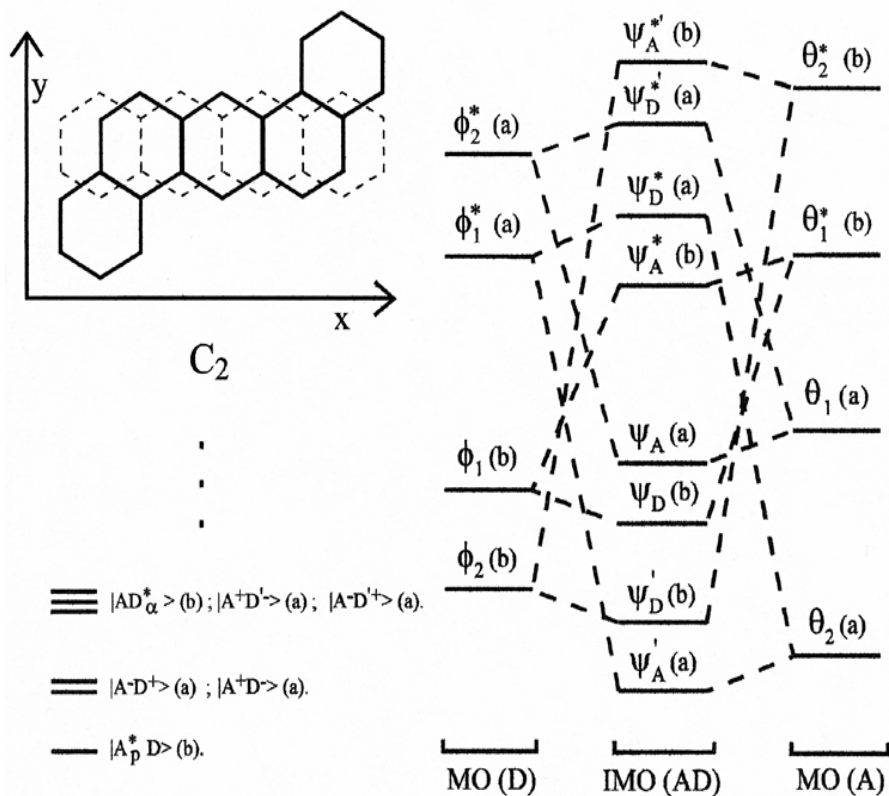
The irreducible  $a_u$  and  $b_g$  representations of  $C_{2h}$  (symmetry point group of chrysene or DBA) are respectively transformed to  $a$  and  $b$  in the  $C_2$  group. The representations  $b_{1u}$ ,  $a_u$ ,  $b_{2g}$  and  $b_{3g}$  of  $D_{2h}$  group (symmetry point group of tetracene) are transformed to  $a$ ,  $a$ ,  $b$  and  $b$  respectively.

Figures 5 and 6 represent these situations. In Figure 5 the correlation between MO of chrysene and tetracene gives rise to a SYN correlation. All electron promotions from bonding  $\Psi_i$  to antibonding  $\Psi_j^*$  give rise to excited zeroth-order configurations which are not totally symmetrical ( $b$  symmetry because  $a \otimes b = b$ ). Thus, none of these configurations

allows the stabilisation of a ground-state complex. In this case the formation of an exciplex appears most likely.



**Figure 5. Schematic diagram of a cofacial C<sub>2</sub> structure between chrysene (D) and tetracene (A). Right: SYN correlation diagram and MO symmetries of complex. Left: relative energy and excited zeroth-order configurations.**



**Figure 6. Schematic diagram of a cofacial C<sub>2</sub> structure between DBA (D) and tetracene (A). Right: ANTI correlation diagram and MO symmetries of complex. Left: relative energy and excited zeroth-order configurations.**

In Figure 6, the most favorable correlations are of the type ANTI: the charge transfer (CT) at zeroth-order configurations (|A<sup>-</sup>D<sup>+</sup>>, |A<sup>+</sup>D<sup>-</sup>>...) are totally symmetric as it is

the case of the ground state configuration  $|AD\rangle$ . Thus a stable complex at the ground state is probable as indicated by configuration interaction (CI). However, the absence of a new absorption band does not remove the above possibility and that of exciplex formation.

#### CONCLUSION

Experimental measurements of mixed aggregates of Tet/Chry and Tet/DBA revealed the formation of an exciplex at high concentrations of the guest species.

The method of correlations proposed by Stevens offered a very good means to investigate the mechanisms that lead through configurations interaction to a stabilisation of the excited state and also of the ground state of the complex.

In the case of Tet/Chry in which no new absorption bands are observed, the formation of an exciplex was shown to be the most probable theoretically. This indicates a remarkable agreement between the theory and the experimental results.

For the Tet/DBA case, the theoretical analysis leads to a stabilisation probability of the complex at the ground state. However, whatever the medium or the phase in which this case has been studied, no absorption bands are observed in order to give evidence for the formation of a complex at the ground state. There thus appears to be a clear indication of an exciplex formation.

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